REMARKS

Status of the Invention.

The present invention relates to an improved process for the bleaching of oxygen delignified kraft pulp using a hemicellulase treatment. Preferably, the hemicellulase has little or no cellulase activity.

Status of the Application.

Claims 1, 4 and 7-13 are pending in this application. Claim 8 stands amended with entry of this Request for Reconsideration. The amendment to claim 8 merely changes the wording of the claim so it is properly dependent on claim 11, a process claim. No new matter has been added with this amendment.

All pending claims stand rejected under 35 USC § 103(a) as allegedly obvious in light of Paice, *et al.*, the "admitted prior art" and Tench, *et al.* with or without du Manoir, *et al.* The claims are rejected as allegedly obvious also in light of Paice, *et al.* in view of Viikarie, *et al.* or Tan, *et al.* and Tench, *et al.* with or without du Manoir, *et al.*

Status of Declaration of Kenneth Madsen under 37 CFR § 1.132.

Applicants have attached a copy of the Declaration of Kenneth Madsen under 37 CFR §1.132. This Declaration was originally filed with the PTO on June 20, 1996 in support of the patentability of the pending claims of USSN 08/514,354, a parent application to the instant application.

35 USC § 103.

The Applicants note that Examiner Alvo has responded to Applicants Preliminary Amendment of June 12, 2000 with exactly the same Office Action as sent before with this additional paragraph:

> Applicant's arguments have been considered, but are not convincing as the specific enzymes would have been obvious to use from the teachings of the ADMITTED PRIOR ART and/or VIIKARI ET AL. and/or TAN ET AL. Applicant has not shown any unexpected results and thus has not overcome the prima facie case of obviousness.

MPEP §707.07 indicates an Examiner's Office Action must be complete and clear. Various form paragraphs are given for use in an Office Action when an Applicant's response has been found not persuasive. Form paragraph 7.37 reads:

> Applicant's arguments filed [1] have been fully considered but they are not persuasive. [2]
> Examiner Note:
> 1. The examiner must address all arguments which have not already been responded to in the statement of the rejection.
> 2. In bracket 2, provide explanation as to non-persuasiveness.

It would appear the Examiner has found Applicant's arguments regarding the other references cited by the Examiner in earlier Office Actions persuasive as they were not included in his explanation (bracket 2). Thus, Applicants respectfully request the rejection under 35 USC § 103(a) in light of Paice, *et al.*, Tench, *et al.* and du Manoir be expressly withdrawn.

In considering obviousness, the prior art as a whole must be considered and its teachings must be viewed as they would have been by one of skill in the art at the time of the invention. To establish a prima facie case of obviousness, the Examiner must cite prior art which discloses each element of the claims unless the element would be obvious to one of skill in the art. The Examiner must also provide reasons or motivation for one of skill to combine the prior art references to carry out the claimed method and demonstrate that one of ordinary skill would have had a reasonable expectation of success in attempting in carrying out the method. *In re Vaeck*, 20 USPQ 2d 1438 (Fed. Cir. 1991).

The Examiner asserts the Applicants have not successfully rebutted a *prima facie* showing of obviousness with unexpected results. The Applicants believe they do not have to as the Examiner has not set forth a *prima facie* case of obviousness. Specifically, nowhere in the Examiner's Office Action has he provided the basis for a reasonable expectation of success. As is well known in the art, enzymes from different organisms have different structures and catalyze under different conditions. From the references cited by the Examiner, there is no way of knowing whether the enzymes of "the admitted prior art," Viikari, *et al.* and/or Tan, *et al.* would be active under the conditions described in the Specification and in fact, ***that they are active is the discovery of the Applicants!*** The Examiner has relied on a circular hindsight analysis; he is stating it is obvious to use the enzymes stated in the Specification because....they were provided

in the specification as being the enzymes the Applicants envisioned using in the claimed invention.

In light of the above remarks, the Applicants believe the pending claims are in condition for allowance and issuance of a formal Notice of Allowance at an early date is respectfully requested. If a telephone conference would expedite prosecution of this application, the Examiner is invited to telephone the undersigned at (650) 846-7609.

Respectfully submitted,

Date: June 6, 2001

Susan Faris
Registration No. 41,739

Genencor International, Inc.
925 Page Mill Road
Palo Alto, CA 94304-1013
Tel: 650 846-7609
Fax: 650 845-6504

APPENDIX I (Pending Claims)

1. (Thrice amended) In a process for the bleaching of oxygen delignified wood derived kraft pulp, the improvement comprising treating the oxygen delignified kraft pulp with a hemicellulose-hydrolyzing enzyme or enzyme preparation, said enzyme being derived from the genus *Trichoderma* or from *Chainia sp.* ATCC 53812 and wherein said enzyme or preparation contains less than 0.5% of cellulase activity.

4. (Twice amended) The process according to claim 1, wherein the hemicellulose-hydrolyzing enzyme is produced by a species belonging to the genus *Trichoderma.*

7. (Once amended) The process according to claim 11, wherein said xylanase is added in an amount of about 0.1 – 100 U/g calculated ont eh dry solids of the pulp.

8. (Twice amended) The [method] process according to claim 11, wherein the xylanase is added in an amount of about 0.5 – 25 U/g calculated on the dry solids of the pulp.

9. (Once amended) The process according to claim 11, wherein said xylanase treatment is carried out within the pH range from about 2 to about 10, at a temperature of from about 10 to about 90°C; and enzyme treatment time from about 10 minutes to 24 hours.

11. The process according to claim 1, wherein said hemicellulose-hydrolyzing enzyme is a xylanase produced by *Chainia sp.* ATCC 53812.

12. The process according to claim 4, wherein the hemicellulose-hydrolyzing enzyme is produced by *Trichoderma longibrachiatum.*

13. The process according to claim 1, wherein the pulp consistency during treatment with hemicellulose-hydrolyzing enzyme or enzyme preparation is 10%.

Attachment for
USSN 08/831,277

DOCKET NO. GC198-5

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of
IIkka Kruus, et al.
Serial No. 08/514,354
Filed: August 3, 1995
For: OXYGEN BLEACHING OF PULP

Group Art Unit: 1303
Examiner: Unassigned

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to: Commissioner of Patents and Trademarks, Washington, D.C. 20231 on

Date: JUNE 20, 1996

Signature: Linda M. Fales

DECLARATION OF KENNETH E. MADSEN

Honorable Commissioner of Patents
and Trademarks
Washington, D.C. 20231

1. I am currently employed as an attorney with the Law offices of Kenyon & Kenyon located in New York, New York.

2. On January 24, 1989, I received at Kenyon & Kenyon in New York, New York, by facsimile a date stamped disclosure of an invention entitled "Improvement of Oxygen Bleaching of Pulp", which disclosure is attached hereto as Annex A. The handwritten interlineations on Annex A were added at a later date, but the entirety of the typewritten text was received and docketed on January 24, 1989.

3. I hereby declare that all statements made on information and belief are believed to be true; and further that these statements are made herein with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Title 18, Section 1001 and that willful false statements may jeopardize the validity of this application and any patent issued thereon.

Signature: [redacted]

Date: Dec. 8, 1995

ANNEX A

To: Mr. Madsen/Kenyon & Kenyon

From: Raili Rinkinen /Finnish Sugar Co. Ltd.

Number of pages including this cover letter: 1 + 8

Message: "IMPROVEMENT OF OXYGEN BLEACHING OF PULP" ("PROCESS II")/KRUUS, Ilkka LAINE, Jaakko and KOLJONEN Marja (Reduction to practice in U.S.A).

NBM
review disclosure and file application upon request.

Dear Mr Madsen,

Our company is performed experimental research in the above. Please find enclosed the declaration of the invention (inventor Ilkka KRUUS Jaakko LAINE and Marja KOLJONEN). Additional experiments will be made possibly in cooperation with a Finnish company and the final decision about term of filing a patent application will be made within the next few months.

The meaning of this letter is to secure our rights and thus the "use in U.S.A."

I will return to the case soon, meanwhile kindly take the necessary actions needed for reduction to practice in U.S.A. in this case.

Kindly confirm that you have received this telefax message.

Regards,

Raili Rinkinen/

\patentit\redkruu2

Postal address: P.O.Box 105, SF-00241 HELSINKI, FINLAND | Visiting address: Kyllikinportti 2, 00240 HELSINKI, FINLAND | Telephone: +358 0 134 411 | Telex: 122174 sucro sf | Telefax: +358 0 1344 1344, +358 0 1344 1311 | Cables: SOKERI

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Eli Rinkinen

IMPROVEMENT OF OXYGEN BLEACHING OF PULP

FIELD OF THE INVENTION

This invention relates to an improvement of oxygen bleaching of pulp by enzyme treatment. Specially this invention relates to the use of hemicellulose hydrolysing enzyme substantially free from cellulosic activity.

BACKGROUND OF THE INVENTION

Oxygen bleaching of pulp in its different forms is known and it has been described e.g. in the publication The Bleaching of Pulp, by Singh R., P., Tappi Press 1979, pages 159 - 209.

Increasing price of energy and the demand of protection of environment have made it desirable to substitute chemical bleaching processes of pulp with processes demanding less energy which additionally would make it possible to turn all or at least the main part of the waste liquor from bleaching plant in the conventional burning process of alkaline cooking. Oxygen bleaching of pulp by using sodium hydroxide as an effective alkaline directly after cooking is used today in many paper mills. This process makes it possible to diminish the amount of chlorine and sodium hydroxide used in bleaching plants and to recycle and burn about half of dry substances of the bleaching plant. Extended oxygen bleaching causes extensive depolymerisation of carbohydrates, that diminishes the paper properties of pulp. For the time being it has not been solved how to make it possible to extend the lignification of pulp by using diminished amounts of chlorine, sodium hydroxide and oxygen and make it possible to burn as much as possible of the spent bleaching liquors.

SUMMARY OF THE INVENTION

The object of this invention is to improve the oxygen bleaching of pulp by means of enzyme treatment. The invention is characterised by adding to oxygen bleaching process hemicellulose dissolving enzyme or enzyme preparation. Preferably hemicellulase enzyme or enzyme preparation is substantially free from cellulosic activity.

SUMMARY OF THE INVENTION

Enzyme treatment can be performed before, after or at the oxygen stage.

Enzymes suited for the application according to the invention include hemicellulases and hemicellulase preparations, especially xylanases, which are substantially free from cellulases. As used herein the term cellulases refers to enzymes which are able to dissolve crystalline cellulose and to liberate therefrom remarkable amounts of sugars or

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oligosaccharides. As known, enzymes referred to in the invention are produced e.g. by actinomycetes (such as Streptomyces olivochromogenesis), bacteria (such as Bacillus sp.) and fungi (such as Penicillium steckii). The enzyme according to the invention can also be obtained in such a way that cellulase/hemicellulase preparation produced by Trichoderma reesei fungi is purified by removing all or the main part of cellulosic activity. The suitable enzyme dosage calculated as xylanase is about 0.1 - 100 U/g d.s of mass, preferably about 0.5 - 25 U/g d.s of mass.

DESCRIPTION OF THE INVENTION

INSERT [A]

The treatment can be carried out within the pH ranges from about 2 to about 10, preferably from about 4 to about 8, depending e.g. on the origin and the properties of the used hemicellulase enzyme. Treating time depends on the enzyme dosage and the treatment conditions, ranging from 10 minutes to one day, preferably from half an hour to 8 hours. The temperature during the enzyme treatment may vary from about 10 °C to about 90 °C, preferably from about 25 to 70 °C.

The xylanase activity of the enzyme preparation was determined as follows:

To 1 ml of xylan solution (1 %, Sigma No: X-0376, prepared in 50 mM Na citrate buffer, pH 5.3), 1 ml of an enzyme suitably diluted in the same buffer was added. The solution was incubated at +50 °C in a water bath for 30 minutes. The reaction was stopped by adding 3 ml of DNS reagent (3.5-dinitrosalicylate reagent) and the colour was developed by cooking the sample for 5 minutes. The absorbance was measured at wave length of 540 nm. One enzyme unit liberates one micromole of reducing sugar calculated as xylose per one minute under the assay conditions.

The cellulase activity of enzyme preparations was determined as filter paper activity (Ghose, T., K. et al., Symposium of Enzymatic Hydrolysis of Cellulose, Bailey M., Enari , T. M., Linko, M., Eds. (SITRA, Aulanko, Finland, 1975), p. 111 to 136):

A piece of filter paper (Whatman 1, 50 mg) was added to 1 ml of acetate buffer (0.05 M NaAc, pH 4.8). 1 ml of a suitably diluted enzyme solution was added. The solution was incubated for one hour at 50 °C. The reaction was stopped by adding 3 ml of DNS reagent, and the colour was developed and measured as in the xylanase determination. One

activity unit liberates 1 micromole of reducing sugars calculated as glucose per one minute.

The method according to the invention will be illustrated by means of the following examples. The meaning of the examples is not to restrict the invention but to show the working of some embodiments according to this invention.
This strain was deposited with the ATCC as no. #53812 on
Enzyme of the example 1 and 2 was prepared by Chainia sp. NCL 82-5-1 strain. Spores of Chainia sp. NCL 82-5-1 strain preserved on PDA slants face was transferred to sterile medium (e.g. 5 % wheat bran, 1 % yeast extract, pH 7.0). The medium was cultured in shaking flasks for about 3 to 5 days at 30 °C in vigorous shaking speed (50 - 100 ml liquid, in 250 ml flask, 200 rpm). The liquid was filtered or centrifuged clear. About 10 U/ml of xylanase was produced when wheat bran was used, more xylanase (at least 25 U/ml) was produced when pure xylan base was used.

The enzyme used in Example 3 was produced by actinomycete Streptomyces olivochromogenesis using the method described in Evaluation of Different Microbial Xylanolytic Systems, Poutanen, K., Rättö M., Puls, J., and Viikari, L., Journal of Biotechnology, 6 (1987) p. 49-60; the activity of enzymes: xylanase 2,500 U/g, cellulase 0 U/g.

Example 1

Oxygen bleaching I of birch pulp

Finnish birch sulphate pulp was bleached, the original kappa number of pulp was 20. Bleaching sequence was O_2-D-E-D-E-D. Chlorine dioxide used comprised about 8 % chlorine.

Control pulp was conventionally bleached but in order to make the conditions as comparable as possible for control pulp "enzyme treating" without enzyme was made, by letting the control pulp to stay at 55 °C and at pH 6 for four hours.

Enzyme treatment of pulp was performed before bleaching in the following conditions:

- temperature:	55 °C
- time:	4 hours
- pH:	6
- consistency:	10 %
- enzyme dosage as xylanase:	25 U/g t.s. of mass

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After enzyme treatment (after incubation of control pulp) pulp was washed and the normal oxygen bleaching was performed. In the oxygen stage following conditions were used:

- temperature:	90 °C
- time:	30 min.
- O_2:	3 bar
- consistence:	10 %
- NaOH:	2 %

In the first chlorine dioxide stage act. chlorine dosage: 0.2 x kappa % dry substance of mass was used. In four last stages the dosages of chemicals were following: E1 0.1 x kappa % d.s. of mass, D1 2,5 % of d.s. of mass, E2 0.8 % d.s. of mass, D2 1.0 % of d.s. of mass. The results of the experiments are shown in Table 1.

Table 1

The results of bleaching/oxygen bleaching I/birch pulp

	Control	Enzyme treated
Kappa number after enzyme treatment	20,3	18,3
Kappa number after oxygen stage	14,8	12,2
Brightness %	90,3	92,1
Viscosity kg/m3	1080	1170
TCl mg/kg	573	500
Yield enzyme treatment + bleaching	91,0	90,7

The time of enzyme treatment was moderate: 4 hours, in spite of that the brightness of the pulp increased very remarkably 1.8 % units, even though the original brightness of the pulp was over 90 %. Additionally there was no yield losses.

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Example 2

Oxygen bleaching II of birch pulp

Finnish birch sulphate pulp was bleached; the original kappa number was 20. As bleaching sequenced O_2-enzyme-D/C-E-D-E-D was used. The amount of chlorine dioxide was 90 % and the amount of chlorine 10 % calculated as active chlorine in D/C stage.

Oxygen stage of pulp was performed by using following conditions:

- temperature:	90 °C
- time:	30 min.
- O_2:	3 bar
- consistency:	10 %
- NaOH:	2 %

After oxygen stage the pulp was divided in two parts. The control pulp was normally bleached but in order to make the conditions of the treatment as comparable as possible for the control pulp the treatment corresponding enzyme treatment was performed without enzyme; the control pulp was left staying at 55 °C and at pH value 6 for four hours.

The enzyme treatment of the pulp was performed after oxygen bleaching before D/C stage by using following conditions:

- temperature:	55 °C
- time:	4 hours
- pH:	6
- consistency:	10 %
- enzyme dosage as xylanase:	25 U/g d.s. of mass.

After enzyme treatment (after letting control pulp stay) the pulp was washed and the final bleaching by using the sequence mentioned above was performed. At D/C stage active chlorine dosage 0.2 x kappa % d.s. of mass was used.

In four last stages the dosages of chemicals were following: E1 0.1 x kappa % d.s. of mass, D1 2.5 % d.s. of pulp, E2 0.8 % d.s. of pulp, D2 1.0 % of d.s. of mass.

The results of the experiments are shown in Table 2.

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January 24, 1989

Table 2

Bleaching experiments/oxygen bleaching II/birch pulp

	Control	Enzyme treated
Kappa number after oxygen stage	14,6	14,6
Kappa number after enzyme treatment	13,6	11,7
Brightness %	89,6	92,1
Viscosity kg/m^3	1015	1045
TCl mg/kg	291	352
Yield enzyme treatment + bleaching	91,8	90,9

The time of enzyme treatment was moderate: 4 hours, in spite of that the brightness increased very remarkably 2.5 % units, even though the original brightness was almost 90 %. Additionally yield loss was insignificant.

Example 3

Oxygen bleaching III of birch pulp

Finnish birch sulphate pulp was bleached according to the Example 1 with that exception that the enzyme prepared by actinomycete was used and in addition the time of the enzyme treatment was 8 hours. The results of the experiments are shown in Table 3.

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Table 3

Bleaching experiments/oxygen bleaching III/birch pulp

	Control	Enzyme treated
Kappa number after enzyme treatment	19,9	18,0
Kappa number after oxygen stage	14,7	12,0
Brightness %	90,2	91,1
Viscosity kg/m	1080	1010
TCl mg/kg	560	510
Yield enzyme treatment - bleaching	91,5	87,7

The enzyme treatment improves the bleaching of pulp.

Specially from the examples 1 and 2 a conclusion can be drawn that the use of the enzyme according to this invention in connection with oxygen bleaching the stages E2 and D2 can be even omitted; this means remarkable savings in investments when building a new bleaching plant.

If still more material dissolved in bleaching will be burned one can from the examples draw a conclusion that the normal target brightness 89 - 90 % can be reached without D/C stage. Then the final bleaching after the enzyme treatment and oxygen stage or after oxygen stage and enzyme treatment can be following: E-D-E-D. That means that even the material dissolved in E1 stage can be lead to be burned.

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Patent claims

1 A method for bleaching of pulp characterised by adding to oxygen bleaching process a pulp hemicellulose- dissolving enzyme or enzyme preparation.

2 A method according to claim 1, characterised in that hemicellulose-dissolving enzyme is substantially free from cellulose dissolving enzyme.

3 A method according to claim 1 or 2, characterised in that the enzyme is added before or after oxygen stage or at the oxygen stage

4 A method according to ~~any of the preceding claims~~ 1, 2 or 3 characterised in that the hemicellulose-dissolving enzyme or enzyme preparation is added in an amount of about 0.1 - 100 U/g calculated on the dry substance of the pulp.

5 A method according to any of ~~the preceding claims~~ 1, 2, 3 or 4 characterised in that the enzyme treatment is carried out within pH range from about 4 to about 8; at about 20 to 90 °C ~~preferably at about 40 to 70 °C~~, the time of enzyme treatment is about 10 min. to 24 h, ~~preferably about 0.5 - 5 h.~~

The method according to claim 4 wherein the enzyme treatment is carried out ~~within the pH range of from about 4 to about 8~~ at about 25 to about 70°C for a time period of from about 0.5 to about 5 hours.

3. A method according to claim 2 wherein said hemicellulase is a ~~xylanase~~ low molecular weight xylanase produced by Cainia sp. ATCC 53812.

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